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(54) Title: COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

(57) Abstract: The invention relates to a bleaching composition a ligand that forms a complex with a transition metal or a transition metal complex thereof, the ligand comprising at least one heteroaromatic substituent, the bleaching composition forming in an aqueous solution an air bleaching medium, the bleaching composition having less than 1 % of a peroxyl species present, characterised in that the bleaching composition comprises an anionic surfactant, wherein the anionic surfactant has critical micelle concentration value of 3×10^{-4} M or less.

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COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATEFIELD OF INVENTION

5 This invention relates to compositions and methods for catalytically bleaching substrates in the absence of a peroxy species using catalysts which bleach via air sourced from the air.

BACKGROUND OF INVENTION

10 Recently it has been found that selected organic molecules (ligands) and complexes may be used in air bleaching. Such ligands and complexes thereof are found, for example in: GB 9906474.3; GB 9907714.1; GB 98309168.7, GB 98309169.5; GB 9027415.0 and GB 9907713.3; DE 19755493; EP 999050;

15 WO-A-9534628; EP-A-458379; EP 0909809; United States Patent 4,728,455; WO-A-98/39098; WO-A-98/39406, WO 9748787, WO 0029537, WO 0052124 and WO0060045.

The ligand may be present as a preformed complex of a ligand and a transition metal. Alternatively, the composition may

20 comprise a free ligand that complexes with a transition metal ion present in tap water or stain on a substrate. The composition may also be formulated as a composition of a free ligand or a transition metal-substitutable metal-ligand

25 complex, and a source of transition metal ion, whereby the complex is formed *in situ* in the wash medium.

Many transition metal complexes have high extinction coefficients in the visible. In this regard, use over time

30 substantially in the absence of a peroxy species may result in some colour deposition on a substrate after repeated

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washing. This colour deposition is indicative of transition metal complex deposition on the substrate. The rate and amount of colour deposition depends upon the nature of the transition metal complex and the substrate being bleached.

5

It is an object of the present invention to provide a composition substantially devoid of a peroxy species with reduced colour deposition.

10 SUMMARY OF INVENTION

The scope of the present invention also extends to the reduction in transition metal complex build-up on a substrate. Hence, the present invention is also applicable to transition metal complexes with low extinction

15 coefficients in the UV-vis.

We have found that polyacrylic fabrics are susceptible to colour deposition when subjected to an air bleaching catalyst in the absence of a peroxy species. We have also
20 found that the use of an air bleaching catalyst in conjunction with anionic surfactants having particular properties serves to reduce colour deposition. We have been unable to find any non-ionic detergents *per se* that provide this effect.

25

The present invention also extends to reducing the deposition or incorporation of a ligand or transition metal catalyst thereof into any medium that the aforementioned species may partition into or bind thereto from an aqueous
30 medium.

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In this regard, the present invention provides a bleaching composition having reduced transition metal complex deposition properties comprising a ligand that forms a complex with a transition metal or a transition metal complex thereof the ligand comprising at least one heteroaromatic substituent, the bleaching composition forming in an aqueous solution an air bleaching medium, the bleaching composition having less than 1%, preferably less than 0.1%, of a peroxy species present, characterised in that the bleaching composition comprises an anionic surfactant, wherein the anionic surfactant has a critical micelle concentration value of 3×10^{-3} M or less.

In another aspect the present invention provides a bleaching composition having reduced transition metal complex deposition properties comprising a ligand that forms a complex with a transition metal or a transition metal complex thereof the ligand, the bleaching composition forming in an aqueous solution an air bleaching medium, the bleaching composition having less than 1%, preferably less than 0.1%, of a peroxy species present, characterised in that the bleaching composition comprises an anionic surfactant, wherein the anionic surfactant has a critical micelle concentration value of 3×10^{-3} M or less together with a base selected from at least at least 5 w/w % sodium carbonate and sodium bicarbonates.

Generally, a surfactant will form a micelle when present in an aqueous solution above a specific concentration that is intrinsic to the surfactant. A micelle is an electrically

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charged colloidal particle or ion, consisting of oriented molecules. Above what is known as the *critical micelle concentration* CMC amphiphilic compounds tend to adopt specific aggregates in aqueous solution. The tendency is to avoid contact between their hydrophobic alkyl chains and the aqueous environment and to form an internal hydrophobic phase. Such compounds can form monomolecular layers [monolayers] at the air-water boundary and bimolecular layers [bilayers] between two aqueous compartments. Micelles are spherically closed monolayers.

The particular property required is that the anionic surfactant used in the present invention is and forms a micelle at a concentration of 3×10^{-3} M and below in an aqueous solution at a temperature of 25°C. One skilled in the art will be aware that the standard CMC is measured in deionized water and that the presence of other components in solution, e.g. surfactants or ions in solution will perturb the CMC value. The CMC values and requirement thereof as described herein are measured under standard conditions (N. M. Van Os, J. R. Haak, and L. A. M. Rupert, *Physico Chemical Properties of Selected Anionic Cationic and Nonionic Surfactants* Elsevier 1993; Kresheck, G. C. *Surfactants-In water a comparative treatise-* (ed. F. Franks) Chapter 2 pp 95-197 Plenum Press 1971, New York; and, Mukerjee, P. and Mysels K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*, NSRDS-NBS 36, National Bureau of Standards. US Gov. Print office 1971, Washington, DC). Accordingly, the present invention provides a bleaching composition having reduced transition metal complex

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deposition properties comprising a ligand that forms a complex with a transition metal, the bleaching composition forming in an aqueous solution an air bleaching medium, the bleaching composition having less than 1%, preferably less than 0.1%, of a peroxy species present, characterised in that the bleaching composition comprises an anionic surfactant, wherein the anionic surfactant has a critical micelle concentration value of 3×10^{-3} M or less.

- 10 The anti-colour deposition property of the selected anionic surfactants is also enhanced by the presence of selected anions, namely carbonates and/or bicarbonates. These anions are preferable provided in the form of the sodium salt.
- 15 The anti-colour deposition property of the selected anionic surfactants is also enhanced by the presence of other surfactants other than anionic surfactants.

A unit dose as used herein is a particular amount of the bleaching composition used for a type of wash. The unit dose may be in the form of a defined volume of powder, granules, liquid or tablet.

- A present invention also provides method of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a bleaching composition as defined herein.

The present invention also extends to a commercial package comprising a bleaching composition according to the present invention together with instructions for its use.

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The scope of the present invention also extends to the reduction in transition metal complex build-up on a substrate. Hence, the present invention is also applicable to transition metal complexes with low extinction coefficients in the UV-vis.

The composition of the present invention, in an air bleaching mode, is preferably substantially devoid of a peroxygen bleach or a peroxy-based or peroxy-generating bleach system. The term "substantially devoid of a peroxygen bleach or a peroxy-based or peroxy-generating bleach system" should be construed within spirit of the invention. It is preferred that the composition has as low a content of a peroxy species present as possible. Nevertheless, autoxidation is something that is very difficult to avoid and as a result small levels of peroxy species may be present. These small levels may be as high as 2% but are preferably below 2%. The level of peroxide present is expressed in mMol of hydroperoxide (-OOH) present per Kg.

The additionally added organic compounds having labile CH's, for example allylic, benzylic, -C(O)H, and -CRH-O-R', are particularly susceptible to autoxidation and hence may contribute more to this level of peroxy species than other components. However the presence of an antioxidant in the composition will likely serve to reduce the presence of adventitious peroxy species by reducing chain reactions. The composition of the present invention bleaches a substrate with at least 10 %, preferably at least 50 % and optimally at least 90 % of any bleaching of the substrate being effected by oxygen sourced from the air.

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When only a peroxyacid is present as a peroxy bleaching species in a bleaching medium with a bleaching catalyst [total peroxy present] = $[RC(O)OOH] + [RC(O)OO^-]$. When a mixture of hydrogen peroxide and peroxyacid are present in this medium [total peroxy present] = $[RC(O)OOH] + [RC(O)OO^-] + [H_2O_2] + [HOO^-]$. In some instances, the peroxy species will be relatively unreactive and hence the dominant conditions for "air bleaching" will be still be met by a relatively high level of peroxy species present. The different peroxy species will react at different rates with an "air bleaching catalyst" but what is essential, for "air bleaching mode" is that $k[air\ cat][peroxy]$ is sufficiently small that $k[air\ cat][O_2]$ dominates to the extent that at least 10 % of any bleaching of the substrate is effected by oxygen sourced from the air when the composition is for use in an air bleaching mode. When the composition is used in a peroxy mode there is sufficient peroxy species present to dominate and suppress "air bleaching" in the medium.

The composition provided by the present invention is such that in an aqueous solution at least 10 %, preferably at least 50 % and optimally at least 90 % of any bleaching of a substrate is effected by oxygen sourced from the air.

25 DETAILED DESCRIPTION OF THE INVENTION

Bleach Catalyst

The bleach catalyst per se may be selected from a wide range of organic molecules (ligands) and complexes thereof. Suitable organic molecules (ligands) and complexes for use with the present invention are found, for example in:

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GB 9906474.3; GB 9907714.1; GB 98309168.7, GB 98309169.5; GB 9027415.0 and GB 9907713.3; DE 19755493; EP 999050; WO-A-9534628; EP-A-458379; EP 0909809; United States Patent 4,728,455; WO-A-98/39098; WO-A-98/39406, WO 9748787,

5 WO 0029537; WO 0052124, and WO0060045 the complexes and organic molecule (ligand) precursors of which are herein incorporated by reference. An example of a preferred catalyst is a transition metal complex of MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-

10 aminoethane) of which the FeCl_2 salt thereof has the following extinction coefficients in acetonitrile: $\epsilon_{381\text{nm}} = 8400 \text{ M}^{-1}\text{cm}^{-1}$ and $\epsilon_{458\text{nm}} = 6400 \text{ M}^{-1}\text{cm}^{-1}$. In contrast to the highly coloured FeCl_2 salt of MeN4Py, 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane manganese (II) chloride has a low

15 absorption in the UV visible. The manganese salts of 1,4,7-trimethyl-1,4,7-triazacyclononane has a strong absorption in the UV visible (the manganese salts in their crystalline state have an intense purple colour). Of the ligands used in the present invention it is preferred that the ligand

20 comprises at least one heteroaromatic substituent, it is preferred that the heteroaromatic substituent is a pyridine substituent, and it is most preferred that the heteroaromatic substituent is a pyridin-2-yl moiety. It is even more preferred if the ligand comprises at least two

25 heteroaromatic substituents, it is preferred that the heteroaromatic substituents are pyridine substituents, and it is most preferred that the heteroaromatic substituents are pyridin-2-yl moieties. Of the ligands detailed above it is preferred that the ligand is other than a cross-bridged

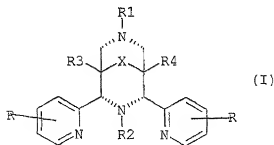
30 macropolycyclic ligand having at least two bridgehead nitrogen donor atoms. The term "a cross-bridged

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macropolycyclic ligand having at least two bridgehead nitrogen donor atoms" will be evident to one skilled in the art but for further direction the reader is directed to WO01/48299.

The air bleaching catalysts as used herein should not be construed as a peroxy-generating system, alone or in combination with other substrates, irrespective of how the bleaching action works.

Another example of an air bleaching catalyst is a ligand or transition metal catalyst thereof of a ligand having the formula (I):



wherein each R is independently selected from: hydrogen, hydroxyl, and C1-C4-alkyl;

R1 and R2 are independently selected from:

C1-C4-alkyl,

C6-C10-aryl, and,

a group containing a heteroatom capable of coordinating to a transition metal, wherein at least one of R1 and R2 is the group containing the heteroatom;

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R3 and R4 are independently selected from hydrogen, C1-C8 alkyl, C1-C8-alkyl-O-C1-C8-alkyl, C1-C8-alkyl-O-C6-C10-aryl, C6-C10-aryl, C1-C8-hydroxyalkyl, and $-(CH_2)_nC(O)OR_5$ wherein R5 is C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,

X is selected from C=O, $-[C(R_6)_2]_Y-$ wherein Y is from 0 to 3 each R6 is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

- 10 It is preferred that the group containing the hetroatom is: a heterocycloalkyl: selected from the group consisting of: pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl; piperazinyl; hexamethylene imine; 1,4-piperazinyl; tetrahydrothiophenyl; tetrahydrofuranlyl; tetrahydropyranlyl;
- 15 and oxazolidinyl, wherein the heterocycloalkyl may be connected to the ligand via any atom in the ring of the selected heterocycloalkyl,
- a. -C1-C6-alkyl-heterocycloalkyl, wherein the heterocycloalkyl of the -C1-C6-heterocycloalkyl is selected
- 20 from the group consisting of: piperidinyl; piperidine; 1,4-piperazine, tetrahydrothiophene; tetrahydrofuran; pyrrolidine; and tetrahydropyran, wherein the heterocycloalkyl may be connected to the -C1-C6-alkyl via any atom in the ring of the selected heterocycloalkyl,
- 25 a -C1-C6-alkyl-heteroaryl, wherein the heteroaryl of the -C1-C6-alkylheteroaryl is selected from the group consisting of: pyridinyl; pyrimidinyl; pyrazinyl; triazolyl; pyridazinyl; 1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl; imidazolyl; pyrazolyl; benzimidazolyl;
- 30 thiazolyl; oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and isoindolyl, wherein the heteroaryl may be connected to the -

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- C1-C6-alkyl via any atom in the ring of the selected heteroaryl and the selected heteroaryl is optionally substituted by -C1-C4-alkyl,
a -C0-C6-alkyl-phenol or thiophenol,
5 a -C2-C4-alkyl-thiol, thioether or alcohol,
a -C2-C4-alkyl-amine, and
a -C2-C4-alkyl-carboxylate.

- The ligand forms a complex with one or more transition
10 metals, in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI.

- 15 The transition metal complex preferably is of the general formula (AI):



- 20 in which:

- M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe (II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably from
25 Fe(II)-(III)-(IV)-(V);

L represents the ligand, preferably N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, or its protonated or deprotonated analogue;

- 30 X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules

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able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

a represents an integer from 1 to 10;

5 k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10;

m represents zero or an integer from 1 to 20.

10 In typical washing compositions the level of the catalyst is such that the in-use level is from 0.1 μ M to 50mM, with preferred in-use levels for domestic laundry operations falling in the range 1 to 10 μ M. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching.

15 Preferably, the aqueous medium has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, still more preferably from pH 8 to 11, and most preferably from pH 8 to 10, in particular from pH 9 to 10.

20 The bleaching composition of the present invention has particular application in detergent formulations, especially for laundry cleaning. Accordingly, in another preferred embodiment, the present invention provides a detergent
25 bleach composition comprising a bleaching composition as defined above and additionally a surface-active material, optionally together with detergency builder.

30 In addition to the requirement of the anionic surfactant, the bleach composition according to the present invention may for example contain additional surface-active material

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- in an amount of from 10 to 50% by weight. The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.
- 10 Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher aryl groups. Examples
- 15 of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear
- 20 secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphonates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphonates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C₉-C₁₈)
- 25 fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane

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monosulphonates such as those derived by reacting alpha-olefins (C₈-C₂₀) with sodium bisulphite and those derived by reacting paraffins with SO₂ and Cl₂ and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium (C₇-C₁₂) dialkyl sulposuccinates; and olefin sulphonates, which term is used to describe material made by reacting olefins, particularly (C₁₀-C₂₀) alpha-olefins, with SO₃ and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C₁₀-C₁₅) alkylbenzene sulphonates, and sodium (C₁₆-C₁₈) alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C₆-C₂₂) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If

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any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

5

The detergent bleach composition of the invention will preferably comprise from 1 to 15% wt of anionic surfactant and from 10 to 40% by weight of nonionic surfactant.

10 The bleach composition of the present invention may also contain a detergency builder, for example in an amount of from about 5 to 80% by weight, preferably from about 10 to 60% by weight.

15 Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include
20 alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic
25 acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

30

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Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts. Typical builders usable in the present invention may be present at up to 30% w/w, and are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

Apart from the components already mentioned, the bleach composition of the present invention can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or

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substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

Transition metal sequestrants such as EDTA, and phosphonic acid derivatives such as EDTMP (ethylene diamine tetra(methylene phosphonate)) may also be included, in addition to the ligand specified, for example to improve the stability sensitive ingredients such as enzymes, fluorescent agents and perfumes, but provided the composition remains bleaching effective. However, the composition according to the present invention containing the ligand, is preferably substantially, and more preferably completely, devoid of transition metal sequestrants (other than the ligand).

The composition may contain additional enzymes as found in WO 01/00768 A1 page 15, line 25 to page 19, line 29, the contents of which are herein incorporated by reference.

EXAMPLES

25 Synthesis

[(MeN4Py)FeCl]₂Cl

The ligand N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane (MeN4py) was prepared as described in EP 0 909 809 A2.

30 The ligand MeN4Py (33.7 g; 88.5 mmoles) was dissolved in dry methanol (500ml). Small portions of FeCl₂.4H₂O (0.95 eq;

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16.7 g; 84.0 mmoles) were added, yielding a clear red solution. After addition, the solution was stirred for 30 minutes at room temperature, after which the methanol was removed (rotary-evaporator). The dry solid was ground and
5 150 ml of ethylacetate was added and the mixture was stirred until a fine red powder was obtained. This powder was washed twice with ethyl acetate, dried in the air and further dried under reduced pressure vacuum at 40 °C. El. Anal. Calc. for
[Fe(MeN4py)Cl]Cl.2H₂O: C 53.03; H 5.16; N 12.89; Cl 13.07;
10 Fe 10.01%. Found C 52.29/ 52.03; H 5.05/5.03; N 12.55/12.61; Cl: 12.73/12.69; Fe: 10.06/10.01%.

Washing Experiments

The following washing experiments were carried out in
15 tergotometer at 25°C using 500ml of test solution.
The test solutions each contained [(MeN4Py)FeCl]Cl catalyst at a concentration of 0.001g in 500ml in addition to the other components at concentrations shown in the following tables. To this solution was added approximately 20g of
20 white knitted acrylic test monitors (15cm x 15cm pieces) whose reflectance had previously been measured and recorded using a Hunterlab Ultrascan XE. Washing of the monitors was then carried out for 30 minutes with continual agitation at 100 revolutions per minute. After washing, the acrylic
25 monitors were wrung out by hand and given a single rinse by immersion in tap water at a liquor to cloth ratio of 100:1. This wash sequence was then repeated a further four times on the same monitor cloths each time with a fresh batch of the same test solution. After rinsing on the final (fifth) wash

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cycle, the monitor cloths were line-dried under ambient laboratory conditions.

When dry, the reflectance of the monitor cloths was re-measured using a Hunterlab Ultrascan XE and the change in reflectance (after wash - before wash) calculated as Delta E (CIELAB). The measured colour difference (ΔE) between the washed cloth and the unwashed cloth is defined as follows:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

wherein ΔL is a measure for the difference in darkness between the washed and unwashed test cloth; Δa and Δb are measures for the difference in redness and yellowness respectively between both cloths. With regard to this colour measurement technique, reference is made to Commission International de l'Eclairage (CIE); Recommendation on Uniform Colour Spaces, colour difference equations, psychometric colour terms, supplement no 2 to CIE Publication, no 15, Colorimetry, Bureau Central de la CIE, Paris 1978.

Table 1 below shows the critical micelle concentration (CMC) values for a series of anionic surfactants.

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Table 1

Soap Surfactant	CMC (25°C)
Sodium Oleate	7.3×10^{-4} M
Sodium Linoleate	1.8×10^{-3} M
Sodium Stearate	1.9×10^{-4} M
Sodium Iso-Stearate	4×10^{-4} M
Sodium Myristate	4.3×10^{-3} M
Sodium Laurate	2×10^{-2} M

Table 2 below shows the ΔE values obtained from a series of wash experiments carried out with different anionic surfactants.

Table 2

Anionic Surfactant	ΔE
Sodium Isosteate (0.25g/500ml)	0.18
Sodium Oleate (0.25g/500ml)	0.6
Sodium Linoleate(0.25g/500ml)	1.7
Sodium Stearate(0.25g/500ml)	4.0
Sodium Myristate(0.25g/500ml)	5.7
Sodium Laurate(0.25g/500ml)	5.8
Water only (control)	6.8

The following Table 3 below shows the CMC of anionic surfactant, molar concentration of anionic surfactant obtained (0.25g/500ml), and ΔE values obtained from the experimental results given above.

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Table 3

Anionic Surfactant	Conc/M	CMC/M	ΔE
Sodium Isostearate	1.63×10^{-3}	4×10^{-4}	0.18
Sodium Oleate	1.64×10^{-3}	7.3×10^{-4}	0.6
Sodium Linoleate	1.65×10^{-3}	1.8×10^{-3}	1.7
Sodium Stearate	1.63×10^{-3}	1.9×10^{-4}	4.0
Sodium Myristate	2.00×10^{-3}	4.3×10^{-3}	5.7
Sodium Laurate	2.50×10^{-3}	2×10^{-2}	5.8
Water only (control)	-	-	6.8

Table 4 below shows the ΔE values obtained for series of wash experiments carried out with different anionic surfactants.

Table 4

Anionic Surfactant	CMC/M	ΔE
Dobanol® 25 S3 (SLES) (0.25g/500ml)	8.5×10^{-4}	2.0
LAS (linear alkyl benzene sulphonate) (0.25g/500ml)	1.5×10^{-3}	4.6
Sodium dodecyl sulphate (0.25g/500ml)	8×10^{-3}	5.9
AOS(alpha-olefin-sulphonate) (0.25g/500ml)	$5-10 \times 10^{-3}$	6.0

The results given in Tables 2 to 4 above are indicative that the presence of an anionic surfactant having a critical micelle concentration value of 3×10^{-3} M or less has a significant effect in reducing colour deposition on fabrics. There was observed a substantial reduction in colour deposition when LAS (CMC = 1.5×10^{-3} M) is used as a surfactant over Sodium Myristate (CMC = 4.3×10^{-3} M). LAS

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and Sodium Myristate straddle the threshold value CMC value of 3×10^{-3} M.

Table 5 below shows the ΔE values obtained for series of wash experiments carried out with different commercially available anionic surfactants (fatty acid mixtures). The fatty acid mixtures were neutralised with sodium hydroxide solution equivalent to the corresponding soap mixtures before use. Prifac® 5916 (ex Unichema®) is a fatty acid mixture containing greater than 70% of fatty acids of chain length less or equal to C14. Priolene® 6907 (ex Unichema®) is a fatty acid mixture containing in excess of 70% oleic acid.

15 Table 5

	ΔE
Prifac® 5916 (0.25g/500ml)	8.2
Priolene® 6907 (0.5g/500ml)	0.6

The results given in Table 5 are indicative that commercial mixture of alkali metal fatty acid anionic surfactants containing the presence of an anionic surfactant having a critical micelle concentration value of 3×10^{-3} M or less may be employed to reduce colour deposition on fabrics.

Table 6 below shows the ΔE values obtained for series of wash experiments carried out with nonionic surfactants.

25

Table 6

Nonionic surfactant	ΔE
Neodol® 25 7EO (0.65g/500ml)	7.4
Imbentin® AG124 S/065 (0.25g/500ml)	6.4

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The results given in Table 6 above are indicative that nonionic surfactants are not effective in reducing colour deposition.

- 5 Table 7 below shows the ΔE values obtained for series of wash experiments carried out with a combination of an anionic and a nonionic surfactant.

Table 7

Anionic/Nonionic Surfactant Mixtures	ΔE
LAS(0.25g/500ml)/ Imbentin® AG124 S/065 (0.25g/500ml)	3.5
Sodium Laurate (0.25g/500ml)/ Imbentin® AG124 S/065 (0.25g/500ml)	3.3

10

The results given in Table 7 above are indicative that the reduced colour deposition due to the presence of an anionic surfactant is enhanced by the presence of a nonionic surfactant. When sodium laurate (0.25g/500ml) is used under similar conditions without another surfactant a ΔE value of 5.8 is obtained as shown in Tables 2 and 3.

15

Table 8 below shows the ΔE values obtained for series of wash experiments carried out with different anionic surfactants at varying concentrations.

20

Table 8

Surfactant Level	Conc/M	ΔE
Water Only	-	6.8
Sodium Oleate (0.02g/500ml)	1.31×10^{-4}	4.7
Sodium Oleate (0.05g/500ml)	3.28×10^{-4}	4.1
Sodium Oleate (0.1g/500ml)	6.57×10^{-4}	2.6
Sodium Oleate (0.25g/500ml)	1.64×10^{-3}	0.6

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Table 9 below shows the ΔE values obtained for series of wash experiments carried out with different inorganic salts, some at varying concentrations.

5 Table 9

Inorganic Salts	ΔE
Sodium Carbonate (0.5g/500ml)	4.9
Sodium Carbonate (0.25g/500ml)	6.2
Sodium Bicarbonate (0.5/500ml)	5.0
Sodium Bicarbonate (0.25g/500ml) 5g/500ml)	6.2
Sodium Tripolyphosphate (0.4g/500ml)	7.5
Tri-sodium Citrate (0.25g/500ml)	6.9
Sodium Acetate (0.25g/500ml)	6.1
Sodium Chloride (0.5g/500ml)	5.9
Sodium Sulphate (0.5g/500ml)	6.1

The results given in Table 9 above are indicative that inorganic salts have an effect in reducing colour deposition. Of the salts tested both carbonate and

10 bicarbonate salts are the most effective in reducing colour deposition.

Table 10 shows the effect of carbonate salts in combination with anionic and nonionic surfactants.

15

Table 10

Components	ΔE
LAS (0.25g/500ml)	4.6
LAS (0.25g/500ml) / Sodium carbonate (0.3g/500ml)	4.0
LAS (0.25g/500ml) / Imbentin® AG124 S/065 (0.25g/500ml) / Carbonate (0.5g/500ml)	2.2

The results given in Table 10 above are indicative that anionic surfactants in combination with a non-ionic
 20 surfactant and an alkali carbonate salt are effective in reducing colour deposition.

- 25 -

Below are provided suitable composition for use with the present invention in which an air bleaching catalyst may be incorporated in the range 0.005 to 0.1 wt/wt %. It is preferred that a unit dose provides in an aqueous wash solution a concentration of a ligand or transition metal thereof (air bleaching catalyst) in the range of 0.5 to 5 μM , most preferably 1 to 2 μM .

Composition formulation A:

component	%
(Coco) PAS (CMC of 2.1×10^{-3} M)	10%
Nonionic surfactant, ethoxylated fatty alcohol type	18.4%
Oleic acid	10%
Deflocculating polymer, polymer A11 from EP346,995	1%
silicon oil to control foam	0.03%
KOH	4.1 %
NaOH	0.9%
Citric acid.H ₂ O	5.5%
Glycerol	5%
Borax	1.9%
Anti-dye transfer polymer	0.3%
Protease	0.3%
Lipolase	0.37%
Amylase	0.15%
Perfume	0.47%

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Composition formulation B:

Component	%
LAS	24
Sodium TripolyPhosphate (STP)	14.5
SCMC	0.33
Acusol 479	1.5
Fluorescer	1.54
Protease	0.94
Lipolase	0.19
Amylase	0.28
Cellulase	0.2
Sodium Carbonate	17.5
Sodium Silicate	6.9
Sodium Sulphate	25
Moisture	To 100%

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CLAIMS:

1. A bleaching composition having reduced transition metal complex deposition properties comprising a ligand that forms
5 a complex with a transition metal or a transition metal complex thereof the ligand comprising at least one heteroaromatic substituent, the bleaching composition forming in an aqueous solution an air bleaching medium, the bleaching composition having less than 1%, preferably less
10 than 0.1%, of a peroxy species present,
characterised in that the bleaching composition comprises an anionic surfactant, wherein the anionic surfactant has a critical micelle concentration value of 3×10^{-3} M or less.
15
2. A bleaching composition according to claim 1, wherein the anionic surfactant has a critical micelle concentration value of 2×10^{-3} M or less.
- 20 3. A bleaching composition according to claim 1, wherein a unit dose of the bleaching composition provides a concentration of the anionic surfactant in an aqueous solution of at least 1×10^{-4} M.
- 25 4. A bleaching composition according to claim 3, wherein a unit dose of the bleaching composition provides a total anionic surfactant concentration in an aqueous solution of at least 5×10^{-4} M.

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5. A bleaching composition according to any preceding claim, wherein the bleaching composition comprises an alkali metal salt of an anion selected from the group consisting of carbonate and bicarbonates, preferably present in the composition at a concentration of at least 5 w/w %.
6. A bleaching composition according to claim 1, wherein a unit dose of the bleaching composition provides a concentration of carbonate in an aqueous solution of at least 1×10^{-3} M.
7. A bleaching composition according to claim 5, wherein the alkali metal salt is sodium.
8. A bleaching composition according to any preceding claim, wherein the bleaching composition comprises a nonionic surfactant, at a level of at least 1 w/w %.
9. A bleaching composition according to any preceding claim, wherein the anionic surfactant is selected from the group consisting of linear alkyl benzene sulphonate (LAS), sodium C12-C15-alkyl ether sulphate, sodium oleate, sodium linoleate, sodium isostearate and sodium Stearate.
10. A bleaching composition according to any preceding claim, wherein the ligand in the form of a transition metal complex selected from group consisting of Fe, Co, or Mn has an extinction coefficient (ϵ) in an acetonitrile solution of at least $2000 \text{ M}^{-1}\text{cm}^{-1}$ within the UV-vis range of 330 nm to 650nm.

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11. A bleaching composition according to any preceding claim, wherein the ligand comprises at least one pyridin-2-yl moiety.
12. A bleaching composition according to any preceding claim, wherein the ligand comprises at least two pyridin-2-yl moieties.
13. A bleaching composition according to any preceding claim, wherein the ligand is other than a cross-bridged macropolycyclic ligand having at least two bridgehead nitrogen donor atoms.
14. A bleaching composition according to any preceding claim, wherein the ligand is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminocethane.
15. A bleaching composition according to any preceding claim, wherein the composition comprises a preformed complex of the ligand and a transition metal.
16. A bleaching composition according to any preceding claim, wherein the ligand is present as a free ligand that complexes with a transition metal selected from the source of: transition metal present in the bleaching composition, adventitious transition metal ions present in tap water, and transition metal ions present in a stain.
17. A bleaching composition according to any preceding claim, comprising a builder.

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18. A method of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a bleaching composition as defined in any preceding claim.

- 5 19. A method for reducing partitioning of a ligand or transition metal complex thereof from an aqueous medium into a substrate, the method comprising the step of treating said substrate with an aqueous solution of said ligand or said transition metal complex thereof in the presence of an
10 anionic surfactant, said anionic surfactant having a critical micelle concentration value of 3×10^{-3} M or less.

20. A bleaching composition having reduced transition metal complex deposition properties comprising a ligand that forms
15 a complex with a transition metal or a transition metal complex thereof, the bleaching composition forming in an aqueous solution an air bleaching medium, the bleaching composition having less than 1%, preferably less than 0.1%, of a peroxy species present, characterised in that the
20 bleaching composition comprises an anionic surfactant, wherein the anionic surfactant has a critical micelle concentration value of 3×10^{-3} M or less together with a base selected from at least at least 5 w/w % sodium carbonate and sodium bicarbonates.

25

21. A bleaching composition according to claim 20, wherein the base is sodium carbonate and the ligand comprises at least one heteroaromatic substituent.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 60043 A (UNILEVER PLC (GB); LEVER HINDUSTAN LTD (IN); UNILEVER NV (NL)) 12 October 2000 (2000-10-12) cited in the application page 1, line 7 - line 12 page 3, line 29 - page 4, line 8 page 5, line 27 - page 17, line 22 claims; examples; tables 1,2	1-7, 9-16, 18-21
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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